STATEMENT

I, Kazuhito INO, a citizen of Japan, residing in Gifu-shi, Gifu-ken, Japan, hereby state that I am the translator of the attached document and I believe it is an accurate translation of Japanese Patent Application No. 2002-379025, filed on December 27, 2002, in the name of NOF CORPORATION.

Kazuhito INO

Translator

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[Inventor]

[Address] 3-16-3, Mohamaryokuen, Mihama-cho, Chita-gun, Aichi

[Name] Yasumasa WATANABE

[Inventor]

[Address] 9-50, Aza-Nagaso, Hibara, Tokoname-shi, Aichi

[Name] Hiroshi OKADA

[Inventor]

[Address] 31-2, Aza-Koyo 1-chome, Taketoyo-cho, Chita-gun, Aichi

[Name] Tomoyuki NAKAMURA

[Applicant for Patent Application]

[Applicant Registration No.] 000004341

[Name] NOF CORPORATION

[Representative] Yohei NAKAMURA

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[Name of Document] Specification 1

[Name of Document] Abstract 1

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Reference Number: 10514021
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[Name of Document] Specification

[Title of the Invention] Method for producing hydroxyl-modified ethylene-α-olefin copolymer

[Claims]

1. A hydroxyl-modified ethylene-α-olefin copolymer production method in which an ethylene-α-olefin copolymer is heated in the presence of a peroxide having a hydroperoxy group, the method being characterized by:

mixing 0.1 to 20 parts by weight of the peroxide having a hydroperoxy group with respect to 100 parts by weight of an ethylene-α-olefin copolymer; and

the heating temperature being between a 10-hour half-life temperature and a 1-minute half-life temperature of the peroxide.

2. A hydroxyl-modified ethylene-α-olefin copolymer production method in which an ethylene-α-olefin copolymer is heated in the presence of a peroxide having a hydroperoxy group and a radical generator having a 1-minute half-life temperature not higher than 195°C, the method being characterized by:

mixing 0.1 to 20 parts by weight of the peroxide having a hydroperoxy group with respect to 100 parts by weight of an ethylene-α-olefin copolymer, and the radical generator so that not more than 1 mole of the radical generating groups are present with respect to 1 mole of the hydroperoxy groups of the peroxide; and

the heating temperature being between a 10-hour half-life temperature of the radical generator and 220°C.

3. The method according to claim 1 or 2, wherein the peroxide having a hydroperoxy group is one of t-butyl hydroperoxide, t-amyl hydroperoxide, t-hexyl hydroperoxide, t-octyl hydroperoxide, cumene hydroperoxide or diisopropylbenzene hydroperoxide.

4. The method according to any one of claims 1 to 3, wherein said mixing is performed in a kneading condition.

5. A hydroxyl-modified ethylene-α-olefin copolymer produced by the method according to any one of claims 1 to 4, the hydroxyl-modified ethylene-α-olefin copolymer containing 0.001 to 1 mole of hydroxyl groups per 1 kg of the hydroxyl-modified ethylene-α-olefin copolymer and having Mooney viscosity of 10 to 250 at 100°C.

6. A hydroxyl-modified ethylene-α-olefin copolymer composition comprising:

the hydroxyl-modified ethylene-α-olefin copolymer according to claim 5; and

at least one member selected from the group consisting of a thermoplastic resin, a filler, an antioxidant, a light stabilizer, a plasticizer, a lubricant, a flame retardant and a colorant.

[Detailed Explanation of the Invention]

[0001]

[Industrial Field of the Invention]

The present invention relates to a method for easily and efficiently producing a hydroxyl-modified ethylene-α-olefin copolymer without cross-linking or degrading an ethylene-α-olefin copolymer, which is a starting material, and to a hydroxyl-modified ethylene-α-olefin copolymer excellent in coatability and adhesiveness.

[0002]

[Prior Art]

Ethylene-α-olefin copolymers such as an ethylene-propylene bipolymer (hereinafter abbreviated as EPM) and ethylene-propylene-nonconjugated diene terpolymer (hereinafter abbreviated as EPDM) are excellent in moldability, mechanical properties, water resistance, weatherability, heat resistance and chemical resistance, and are therefore being used in many fields of, for example, car components, home electric appliances and office equipment. In addition, since thermoplastic elastomers obtained by blending an ethylene-α-

olefin copolymer and polyolefin resin such as polypropylene and polyethylene have excellent properties and recyclability, they are now attracting attention mainly in terms of applications to automobiles.

[0003]

However, ethylene-α-olefin copolymers and the aforementioned thermoplastic elastomers have a defect that because they do not have a polar functional group in the molecule, their affinity with other substances is poor, and thus the coatability and the adhesiveness are quite inferior.

To overcome the above defect, an attempt to introduce a hydroxyl group, which is a polar functional group, into the structure of an ethylene-α-olefin copolymer, that is, to modify the ethylene-α-olefin copolymer with hydroxyl groups, has been variously studied. For example, a method comprising epoxidizing a double bond in EPDM using hydrogen peroxide and then conducting hydrolysis has been disclosed (e.g., see Patent Document 1). Furthermore, a method of grafting in which a vinyl monomer having a hydroxyl group, such as 2-hydroxyethyl methacrylate, is reacted with a mixture of EPM and polypropylene in the presence of a radical generator such as dialkyl peroxide has been proposed (e.g., see Patent Document 2).

[0004]

[Patent Document 1] Japanese Patent Laid-Open Publication No. 9-241448 (p.7)

[0005]

[Patent Document 2] Japanese Patent Laid-Open Publication No. 3-258845 (pp.4 to 5)

[0006]

[Problems that the Invention is to Solve]

However, the method described in Patent Document 1 is a two-stage process, which also requires use of a great amount of organic solvent such as toluene to dissolve EPDM, and the

method was thus complex and economically disadvantageous. In addition, the method had an essential problem that it cannot be applied to ethylene-α-olefin copolymers which do not contain a double bond.

In addition, the method described in Patent Document 2 had a problem that because polymer radicals produced by a radical generator such as dialkyl peroxide react with each other to be cross-linked, or suffer from decomposition before reacting with a vinyl monomer to cross-link or degrade the resin, thereby damaging the processability and the properties of the resin. Further, because of occurrence of homopolymerization of vinyl monomers or loss of ester moieties to which a hydroxyl group is bonded caused by hydrolysis, it was also difficult to introduce a hydroxyl group efficiently.

[0007]

The present invention has been made in view of the problems of conventional arts, and an object of the present invention is to provide a method for easily and efficiently producing a hydroxyl-modified ethylene-α-olefin copolymer without cross-linking or degrading an ethylene-α-olefin copolymer, which is a starting material, and to a hydroxyl-modified ethylene-α-olefin copolymer excellent in coatability and adhesiveness.

[0008]

[Means for Solving the Problems]

The inventors of the present invention have conducted intensive studies to achieve the above-mentioned object and have found that an ethylene-α-olefin copolymer can be efficiently hydroxylated by mixing a specific peroxide with the copolymer and heating them, whereby a hydroxyl-modified ethylene-α-olefin copolymer excellent in coatability and adhesiveness can be obtained, and the present invention has been completed.

[0009]

The first invention is a hydroxyl-modified ethylene-α-olefin copolymer production method in which an ethylene-α-olefin copolymer is heated in the presence of a peroxide having a hydroperoxy group, the method being characterized by mixing 0.1 to 20 parts by weight of the peroxide having a hydroperoxy group with respect to 100 parts by weight of an ethylene-α-olefin copolymer; and the heating temperature being between a 10-hour half-life temperature and a 1-minute half-life temperature of the peroxide.

The second invention is a hydroxyl-modified ethylene-α-olefin copolymer production method in which an ethylene-α-olefin copolymer is heated in the presence of a peroxide having a hydroperoxy group and a radical generator having a 1-minute half-life temperature not higher than 195°C, the method being characterized by mixing 0.1 to 20 parts by weight of the peroxide having a hydroperoxy group with respect to 100 parts by weight of an ethylene-α-olefin copolymer, and the radical generator so that not more than 1 mole of the radical generating groups are present with respect to 1 mole of the hydroperoxy groups of the peroxide; and the heating temperature being between a 10-hour half-life temperature of the radical generator and 220°C.

[0010]

The third invention is the method according to the first or second inventions, wherein the peroxide having a hydroperoxy group is one of t-butyl hydroperoxide, t-amyl hydroperoxide, t-hexyl hydroperoxide, t-octyl hydroperoxide, cumene hydroperoxide or diisopropylbenzene hydroperoxide.

[0011]

The fourth invention is the method according to any one of the first, second and third inventions, wherein said mixing is performed in a kneading condition.

The fifth invention is a hydroxyl-modified ethylene-α-olefin copolymer produced by the method according to any one of

claims 1 to 4, the hydroxyl-modified ethylene-α-olefin copolymer containing 0.001 to 1 mole of hydroxyl groups per 1 kg of the hydroxyl-modified ethylene-α-olefin copolymer and having Mooney viscosity of 10 to 250 at 100°C.

The sixth invention is a hydroxyl-modified ethylene-α-olefin copolymer composition comprising the hydroxyl-modified ethylene-α-olefin copolymer according to the fifth invention; and at least one member selected from the group consisting of a thermoplastic resin, a filler, an antioxidant, a light stabilizer, a plasticizer, a lubricant, a flame retardant and a colorant.

[0012]

[Embodiments according to the Present Invention]

In the following, embodiments of the present invention are described in detail.

The present invention relates to a method for producing a hydroxyl-modified ethylene-α-olefin copolymer, which includes a step of heating an ethylene-α-olefin copolymer in the presence of a peroxide having a hydroperoxy group.

[0013]

The ethylene-α-olefin copolymer used in the present invention is a copolymer of ethylene and α-olefin, and a copolymer of ethylene-α-olefin-nonconjugated diene.

Examples of the α-olefin include α-olefins having 3 to 20 carbon atoms such as propylene, butene-1, pentene-1, 2-methylbutene-1, 3-methylbutene-1, hexene-1, 3-methylpentene-1, 4-methylpentene-1, 3,3-dimethylbutene-1, heptene-1, methylhexene-1, dimethylpentene-1, trimethylbutene-1, ethylpentene-1, octene-1, methylpentene-1, dimethylhexene-1, trimethylpentene-1, ethylhexene-1, methylethylpentene-1, diethylbutene-1, propylpentene-1, decene-1, methylnonene-1, dimethyloctene-1, trimethylheptene-1, ethyloctene-1, methylethylheptene-1, diethylhexene-1, dodecene-1, tetradecene-1, hexadecene-1, octadecene-1 and eicosane-1. These may be used

alone or in a combination of two or more. Of these, preferred is propylene in that hydroxyl groups can be efficiently introduced by hydrogen abstraction.

[0014]

Examples of the nonconjugated diene include 5-ethylidene-2-norbornene, dicyclopentadiene, tricyclopentadiene, 5-methyl-2,5-norbornadiene, 5-methylene-2-norbornene, 5-isopropenyl-2-norbornene, 5-(1-butenyl)-2-norbornene, cyclooctadiene, vinylcyclohexene, 1,5,9-cyclododecatriene, 6-methyl-4,7,8,9-tetrahydroindene, 2,2'-dicyclopentenyl, trans-1,2-divinylcyclobutane, 2-methyl-1,4-hexadiene, 1,6-octadiene, 1,7-octadiene, 1,4-hexadiene, 1,8-nonadiene, 1,9-decadiene, 3,6-dimethyl 1,7-octadiene, 4,5-dimethyl-1,7-octadiene, 1,4,7-octatriene, 5-methyl-1,8-nonadiene, dicyclooctadiene, methylenenorbornene and 5-vinyl-2-norbornenesan. These may be used alone or in a combination of two or more.

[0015]

Of these nonconjugated dienes, preferred are 5-ethylidene-2-norbornene, dicyclopentadiene and 1,9-decadiene, and particularly preferred are 5-ethylidene-2-norbornene and dicyclopentadiene.

Of such ethylene-α-olefin copolymers, an ethylene-propylene copolymer and an ethylene-propylene-5-ethylidene-2-norbornene copolymer are preferable in that hydroxyl groups can be efficiently introduced by hydrogen abstraction.

[0016]

The proportion of use of each component of the ethylene-α-olefin copolymer is not particularly limited, but those with a weight fraction of each component of 0.2-0.8/0.2-0.8/0-0.2 (described in the order of ethylene/α-olefin/nonconjugated diene, unit: weight ratio) are preferable from the viewpoint that cross-linking or degradation occurs less frequently.

[0017]

The peroxide having a hydroperoxy group used in the

present invention refers to a peroxide having OOH group(s) in its molecule when expressed in chemical structural formula. Examples of the peroxide having a hydroperoxy group include hydrogen peroxide, ketone peroxides such as methyl ethyl ketone peroxide, cyclohexanone peroxide and methylcyclohexanone peroxide; hydroperoxides such as t-butyl hydroperoxide, t-amyl hydroperoxide, t-hexyl hydroperoxide, t-octyl hydroperoxide, 2,5-dimethyl-2,5-dihydroperoxy hexane, cumene hydroperoxide, diisopropylbenzene monohydroperoxide, diisopropylbenzene dihydroperoxide, p-menthan hydroperoxide and pinane hydroperoxide; and organic peracids such as perbenzoic acid and metachloroperbenzoic acid. These may be used alone or in a combination of two or more.

[0018]

Of these, hydroperoxides are preferable, and t-butyl hydroperoxide, t-amyl hydroperoxide, t-hexyl hydroperoxide, t-octyl hydroperoxide, cumene hydroperoxide and diisopropylbenzene hydroperoxide are particularly preferable, because they can be easily melted with or dissolved in an ethylene-α-olefin copolymer and thus the efficiency of introducing hydroxyl groups is high.

[0019]

The amount to be used of the above-mentioned peroxide having a hydroperoxy group is in the range of usually 0.1 to 20 parts by weight, preferably 0.5 to 10 parts by weight with respect to 100 parts by weight of the ethylene-α-olefin copolymer. When the amount to be used of the peroxide having a hydroperoxy group is less than 0.1 part by weight, the amount of the hydroxyl groups introduced becomes small and therefore the effect of modifying an ethylene-α-olefin copolymer is insufficient. On the other hand, when the amount to be used of the peroxide having a hydroperoxy group is more than 20 parts by weight, cross-linking or degradation of the ethylene-α-olefin copolymer tends to occur easily.

The above-mentioned peroxide having a hydroperoxy group can be used by diluting with a solvent such as toluene, cumene or water, or an inert solid such as silica, as well as in a purified form.

[0020]

In the present invention, by using the above-mentioned peroxide having a hydroperoxy group and a radical generator having a 1-minute half-life temperature not higher than 195°C, preferably having a 1-minute half-life temperature of 90 to 190°C together, the heating temperature can be advantageously lowered. The term, 1-minute half-life temperature, refers to a temperature at which the initial concentration of the radical generator is halved in 1 minute, and this can be measured in a diluted solution of benzene etc.

[0021]

Specific examples of the radical generator having a 1-minute half-life temperature not higher than 195°C include dialkyl peroxides such as di-t-butyl peroxide, di-t-amyl peroxide, di-t-hexyl peroxide, t-butyl cumyl peroxide, t-amylcumyl peroxide, t-hexylcumyl peroxide, dicumyl peroxide, α,α'-bis(t-butylperoxy)diisopropyl benezene, and 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane; peroxyketals such as n-butyl-4,4-bis(t-butylperoxy) valerate, 2,2-bis(t-butylperoxy)butane, 1,1-bis(t-butylperoxy)cyclohexane, 1,1-bis(t-hexylperoxy)cyclohexane, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(t-hexylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(t-butylperoxy)-2-methylcyclohexane, and 2,2-bis(4,4-di-t-butylperoxycyclohexyl) propane; peroxy esters such as t-butyl peroxybenzoate, t-amyl peroxybenzoate, t-hexyl peroxybenzoate, t-butyl peroxyacetate, 2,5dimethyl-2,5-bus(benzoilperoxy)hexane, 2,5-dimethyl-2,5-bis(m-torylperoxy) hexane, t-butyl peroxylaurate, t-butyl peroxy-3,3,5-trimethylhexanoate, t-butyl peroxymaleic acid, t-butyl peroxyisobutyrate, t-butyl peroxy-2-ethylhexanoate, t-

hexylperoxy-2-ethylhexanoate, 1,1,3,3,-tetramethylbutylperoxy-2-ethyl hexanoate, t-butyl peroxypivalate, t-hexyl peroxypivalate, t-butyl peroxyneodecanoate, t-hexyl peroxyneodecanoate, 1,1,3,3-tetramethylbutylperoxy neodecanoate and cumyl peroxyneodecanoate; peroxymonocarbonates such as t-butyl peroxy-2-ethylhexyl monocarbonate, t-amylperoxy-2-ethylhexyl monocarbonate, t-hexyl peroxy-2-ethylhexylmonocarbonate, t-butyl peroxyisopropylmonocarbonate, t-amylperoxyisopropylmonocarbonate, and t-hexyl peroxyisopropyl monocarbonate; diacyl peroxides such as benzoyl peroxide, 4-methylbenzoyl peroxide, lauroyl peroxide and 3,3,5-trimethyl hexanoyl peroxide; peroxydicarbonates such as bis(2-ethylhexyl)peroxydicarbonate, bis(2-ethoxyethyl)peroxydicarbonate, bis(4-t-butylcyclohexyl)peroxydicarbonate, dicyclohexyl peroxydicarbonate, di-sec-butyl peroxydicarbonateand diisopropyl peroxydicarbonate; and azo compounds such as 2,2'-azobis(isobutylonitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(2,4-dimethyl 4-methoxyvaleronitrile), 1,1'-azobis(cyclohexane carbonitrile) and 2-(t-butylazo)-2-methylbutanenitrile. These may be used alone or in a combination of two or more.

[0022]

Of the radical generators, preferred are organic peroxides, and particularly preferred are those which have a high radical generation efficiency and a high hydrogen abstraction ability, such as di-t-butylperoxide,t-butylcumyl peroxide, dicumyl peroxide, α,α'-bis(t-butylperoxy)diisopropylbenzene, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane, 1,1-bis(t-butylperoxy)cyclohexane, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, t-butylperoxybenzoate, t-butyl peroxy-2-ethylhexylmonocarbonate, t-butyl peroxy isopropylmonocarbonate, benzoyl peroxide, 4-methylbenzoyl peroxide, bis(2-ethylhexyl)peroxydicarbonate,

bis(4-t-butylcyclohexyl)peroxydicarbonate, dicyclohexylperoxydicarbonate, di-sec-butyl peroxydicarbonate and diisopropyl peroxydicarbonate.

[0023]

The amount to be used of the radical generator is such that not more than 1 mole, preferably not more than 0.8 mole of radical generating groups are present with respect to 1 mole of the hydroperoxy groups of the aforementioned peroxide. When more than 1 mole of radical generating groups are present, side reactions such as cross-linking and degradation tend to occur easily due to polymer radicals generated by the radical generator.

The term, radical generating group(s), refers to a peroxy bond when the radical generator is an organic peroxide, and an azo bond when the radical generator is an azo compound.

[0024]

In the present invention, the method of mixing each component is not particularly limited and includes all known methods. Specific examples of the method include a method of using an apparatus for mechanical mixing such as a Henschel mixer, a method of forming a solution using a solvent including saturated aliphatic hydrocarbons such as n-hexane, n-heptane, isooctane, cyclohexane and cyclopentane; aromatic hydrocarbons such as benzene, toluene and xylene; and halogenated hydrocarbons such as chlorobenzene, dichloromethane and methylene chloride, and a method of kneading using a roll, a kneader, a kneader-ruder, a Banbury mixer or an extruder.

Of these methods, the method of preparing a mixture by kneading is preferable from the viewpoint of economical efficiency, the property of homogeneous mixing and the avoidance of side reactions in which a solvent is involved, such as a reaction in which hydroxyl groups are introduced to a solvent.

[0025]

The method of heating is not particularly limited, but for example, heating is conducted by using a melt kneader or a hot press. For the melt kneader, an apparatus in which kneading means such as a uniaxial or biaxial extruder, a Banbury mixer, a kneader, a kneader ruder or a roll is combined with heating means may be used. In that case, for the timing of heating, heating may be conducted simultaneously with mixing or after kneading according to need.

[0026]

When only using a peroxide having a hydroperoxy group, the heating temperature may be from a 10-hour half-life temperature to a 1-minute half-life temperature of the peroxide having a hydroperoxy group, which is preferably 140 to 250°C.

The term, 10-hour half-life temperature, refers to a temperature at which the initial concentrations of the peroxide and the radical generator are halved in 10 hours, and these can be measured in a diluted solution of benzene etc. When the heating temperature is lower than the 10-hour half-life temperature, the rate of decomposing the peroxide having a hydroperoxy group is low and therefore the efficiency of introducing hydroxyl groups tends to be lowered. On the other hand, when the heating temperature is higher than the 1-minute half-life temperature, the ethylene-α-olefin copolymer may be decomposed.

[0027]

The heating temperature in the case of using peroxide and a radical generator together is from a 10-hour half-life temperature of the radical generator to 220°C, preferably 50 to 200°C. When the heating temperature is lower than the 10-hour half-life temperature, the rate of generating radicals of the radical generator is low and therefore the efficiency of introducing hydroxyl groups tends to be lowered. In addition, when the heating temperature is higher than 220°C, the efficiency of introducing hydroxyl groups also tends to be

lowered because the radical generator decomposes rapidly.

[0028]

In the present invention, by adding, within the range that the object of the present invention is not damaged, at least one member selected from the group consisting of a thermoplastic resin, a filler, an antioxidant, a light stabilizer, a plasticizer, a lubricant, a flame retardant and a colorant to a hydroxyl-modified ethylene-α-olefin copolymer, a hydroxyl-modified ethylene-α-olefin copolymer composition to which a desired property suitable for purposes of use is imparted can be produced. The amount to be added is usually not more than 80% by weight, preferably not more than 50% by weight with respect to the composition.

[0029]

Examples of the thermoplastic resin include polyolefins such as polyethylene and polypropylene.

[0030]

Examples of the filler include natural silica such as diatom earth and silica powder; synthetic silica (white carbon or silica) such as anhydrous silicic acid and hydrated silicic acid; natural silicate such as talc, hard clay, soft clay, sintered clay, pyrophyllite clay, and sericite; metal salts such as heavy calcium carbonate, light calcium carbonate, magnesium carbonate, barium sulfate, gibbsite, bayerite, boehmite, diaspore; and extremely fine activated calcium carbonate and carbon black.

[0031]

Examples of the antioxidant include phenol antioxidants such as 2,6-di-t-butyl-p-cresol, , 3-t-butyl-4-methoxyphenol, 2,6-di-t-butyl-4-ethylphenol, stearyl-β-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, 2,2′-methylenebis(4-methyl-6-t-butylphenol), 2,2′-methylenebis(4-ethyl-6-t-butylphenol), 4,4′-thiobis(3-methyl-6-t-butylphenol), 2,2′-thiobis(6-t-buthyl-o-cresol), 2,2′-thiobis-(6-t-butyl-4-methylphenol), 4,4′-

butylidenebis(3-methyl6-t-buthylphenol), 3,9-bis[1,1-dimethyl-2-[β-(3-t-buthyl-4-hydroxy-5-methylphenyl) propionyloxy]ethyl]2,4,8,10-tetraoxa spiro [5,5]undecane, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benxene, tetrakis-[methylene-3-(3′,5′-di-t-butyl-4′-hydroxyphenyl) propionate]methane, bis[3,3′-bis-[4′-hydroxy-3′-t-butylphenyl) butylic acid]glycol ester, 1,3,5-tris(3,5′-di-t-butyl-4′-hydroxybenxyl)-S-triazine-2,4,6-(1H,3H,5H)trione, 2,4-bis(octylthio)-6-(4-hydroxy-3,5-di-t-butylanilino)-1,3,5-triazine, d-α-tocophenol(α-vitamin E); amine antioxidants such as phenyl β-naphthyl amine and α-naphthyl amine; sulfur antioxidants such as dilauryl thiodipropionate and distearyl thiodipropionate; and phosphorus antioxidants such as triphenyl phosphite, tris(nonylphenyl) phosphite, distearylpentaerythritol diphosphite, and tetra(tridecyl)-1,1,3-trus(2-methyl-5-t-butyl-4-hydroxyphenyl)butane diphospite.

[0032]

Examples of the light stabilizer include salicylic acid stabilizers such as phenyl salicylate and p-octylsalicylate; and benzophenone stabilizers such as 2,4-dihydroxybenxophenone and 2-hydroxy-4-methoxybenzophenone; benzotriazole stabilizers such as 2-(2′-hydroxy-5′-methylphenyl)benzotriazole and 2-(2′-hydroxy-4′-n-octyloxyphenyl)benzotriazole; and resorcinol monobenzoate.

[0033]

Examples of the plasticizer include phthalate esters such as di-2-ethylhexyl phthalate, aliphatic dibasic esters such as di-2-ethylhexyl adipate, phosphate esters such as tributyl phosphate and process oils such as paraffin oil, aromatic oil and naphthene oil.

[0034]

Examples of the lubricant include hydrocarbons such as

liquid paraffin, fatty acids such as stearic acid, fatty acid amides such as stearic acid amide, esters such as butyl stearate, alcohols such as stearyl alcohol, a mixture of these, and metal soap.

[0035]

Examples of the colorant include carbon black, titanium oxide, zinc oxide, red iron oxide, ultramarine blue pigment, Prussianblue pigment, azo pigment, nitroso pigment, lake pigment and phthalocyanine pigment.

[0036]

Examples of the flame retardant include halogen flame retardants such as chlorinated paraffin, chlorinated polyethylene, tetrabromobisphenol A, decabromodiphenyloxide and combination use of these and antimony trioxide; phosphate ester flame retardants such as trischloroethylphosphate, triphenylphosphate, tricresyl phosphate and trixylenylphosphate; and inorganic flame retardants such as magnesium hydroxide.

[0037]

The amount of hydroxyl groups introduced by the method of production of the present invention is preferably 0.001 to 1 mole, more preferably 0.005 to 1 mole per 1 kg of the hydroxyl-modified ethylene-α-olefin copolymer. The Mooney viscosity (ML_{1+4}) of the modified copolymer at 100°C is preferably 10 to 250, more preferably 15 to 200.

The hydroxyl-modified ethylene-α-olefin copolymer may be used as it is, but depending on the type of use or intended properties, it may be cross-linked, mixed with a different polymer, or mixed with such polymer while being cross-linked before it is used. For example, when the copolymer is mixed with or cross-linked while mixing with polyolefin such as propylene or polyethylene, the product may be used for automobile components or electric components.

[0038]

Effects

In the present invention, the following mechanism of introducing hydroxyl groups to an ethylene-α-olefin copolymer can be presumed. Part of peroxides containing a hydroperoxy group(s) is decomposed by heating to generate oxygen-centered radicals which have a hydrogen abstraction ability. They abstract hydrogen from the ethylene-α-olefin copolymer to generate radicals of the ethylene-α-olefin copolymer. As the radicals of the ethylene-α-olefin copolymer attack the peroxide bond of the peroxide having a hydroperoxy group, that is, as induced decomposition occurs, hydroxyl groups are introduced to the ethylene-α-olefin copolymer. In short, according to the radical reaction, hydrogen atoms of the ethylene-α-olefin copolymer are replaced by hydroxyl groups of the peroxide having a hydroperoxy group. When the induced decomposition occurs, the reaction seems to progress as a chain reaction process because it involves generation of radicals having hydrogen abstraction ability.

By using a radical generator having a 1-minute half-life temperature not higher than 195°C in combination, the temperature of chain initiation can be lowered, and therefore when introduction of hydroxyl groups at a lower temperature is intended, such combination use is preferable.

[0039]

[Example]

Next, Examples and Comparative Examples of the present invention will be described. Part(s) and % described below are part(s) by weight and % by weight unless otherwise noted. Abbreviations in each Example indicate the following compounds.
TBHP: t-butyl hydropeoxide (available from NOF Corporation, product name: Perbutyl H-69, purity: 69%, 10-hour half-life temperature: 167°C, 1-minute half-life temperature: 261°C)
CHP: cumene hydroperoxide (available from NOF Corporation, product name: Percumyl H-80, purity: 80%, 10-hour half-life

temperature: 158°C, 1-minute half-life temperature: 254°C)
Perhexa 3M: 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane (available from NOF Corporation, product name: Perhexa 3M, purity: 90%, 10-hour half-life temperature: 90°C, 1-minute half-life temperature: 149°C)

[0040]

EPM: ethylene-propylene copolymer (available from JSR Corporation, product name: JSR EP11, Mooney viscosity ML_{1+4} (100°C): 40)
EPDM: ethylene-propylene-5-ethylidene-2-norbornene copolymer (available from JSR Corporation, product name: JSR EP21, Mooney viscosity ML_{1+4} (100°C): 38)
PP: polypropylene (available from Idemitsu Petrochemical Co., Ltd., product name: J-5066HP)

[0041]

Measuring method of amount of introduced hydroxyl groups

To a flask was added 20 ml of xylene, 0.5 g of a heat-treated polymer sample, 0.4 g of acetic anhydride and 0.2 g of dimethylaminopyridine. The mixture was heated under reflux with stirring for about 30 minutes to dissolve the sample and conduct acetylation thereof.

The xylene solution was put in a large amount of methanol to reprecipitate the polymer. The reprecipitated polymer was dissolved in hot xylene and the mixture was added to methanol and reprecipitated. After drying the reprecipitated polymer, the dried polymer was formed into a film and the infrared absorption spectrum (IR) was measured. Based on the signal at 1740cm^{-1} which suggests esterification of hydroxyl group, the amount of hydroxyl groups introduced to the polymer was quantitatively measured.

[0042]

Example 1

To 100 parts of EPM was added 2.6 parts of TBHP, and the mixture was kneaded by using a roll kneader to give a

composition. The composition was heat-treated at 200°C for 30 minutes by using a pressing machine.

The Mooney viscosity of the heated material was then measured at 100°C. A portion of the heated material was taken to measure the amount of the hydroxyl groups introduced. The results are shown in Table 1.

[0043]

Examples 2 to 4

Experiment was conducted in accordance with Example 1 except that the kind and the amount of addition of peroxide in Example 1 were changed as shown in Table 1. The results are shown in Table 1.

[0044]

Comparative Example 1

Experiment was conducted in accordance with Example 1 except that TBHP was not added. The results are shown in Table 1.

[0045]

Comparative Example 2

Experiment was conducted in accordance with Example 1 except that 1.7 parts of Perhexa 3M was used instead of TBHP in Example 1. The results are shown in Table 1.

[0046]

Table 1

	Per-oxide	Amount added (parts by weight)	ML_{1+4} at 100 °C	amount of hydroxyl groups introduced (mol/kg)
Ex.1	TBHP	2.6	35	0.031
Ex.2	TBHP	1.3	37	0.022
Ex.3	CHP	1.9	38	0.024
Ex.4	CHP	3.8	32	0.031
Comp.Ex.1	-	-	38	0
Comp.Ex.2	3M	1.7	incapable measurement	-

[0047]

Note: In Table 1, the amount of addition is indicated by part(s) by weight with respect to 100 parts by weight of EPM.

In Comparative Example 2, the heated material was cross-linked and it was impossible to measure the Mooney viscosity.

[0048]

The results in Table 1 suggest that when a peroxide with no hydroperoxy group is used (Comparative Example 2), cross-linking remarkably progressed; on the other hand, when a specific peroxide having a hydroperoxy group according to the present invention is used (Examples 1 to 4), hydroxyl groups are efficiently introduced with Mooney viscosity almost the same as that of the material to which peroxide was not added (Comparative Example 1). In other words, it has been found that hydroxyl groups can be introduced almost without cross-linking or degradation.

[0049]

Example 5

By using a roll kneader, 2.6 parts of TBHP and 1.7 parts of Perhexa 3M were added to 100 parts of EPDM and the mixture was kneaded. The obtained composition was heat-treated at 140°C for 30 minutes by using a pressing machine.

The Mooney viscosity of the heated material was then measured at 100°C. A portion of the heated material was taken to measure the amount of the hydroxyl groups introduced. The results are shown in Table 2.

[0050]

Examples 6 to 8

Experiment was conducted in accordance with Example 5 except that the kind and the amount of addition of peroxide in Example 5 were changed as shown in Table 2. The results are shown in Table 2.

[0051]

Comparative Example 3

Experiment was conducted in accordance with Example 5 except that TBHP and 3M were not added. The results are shown in Table 2.

[0052]

Comparative Example 4

Experiment was conducted in accordance with Example 5 except that the amounts of addition of TBHP and 3M in Example 5 were changed as in Table 2. The results are shown in Table 2.

[0053]

Table 2

	Peroxide & Radical generator	Amount added (parts)	Molar ratio	ML_{1+4} at 100 °C	amount of hydroxyl groups introduced (mol/kg)
Ex.5	TBHP 3M	2.6 1.7	1 0.51	36	0.027
Ex.6	TBHP 3M	3.9 1.7	1 0.34	37	0.038
Ex.7	CHP 3M	3.8 0.4	1 0.12	30	0.026
Ex.8	CHP 3M	3.8 1.7	1 0.51	40	0.109
Comp.Ex.3	-	-	-	35	0
Comp.Ex.4	TBHP 3M	2.6 5.0	1 1.49	incapable measurement	-

[0054]

Note: In Table 2, the amount of addition is indicated by part(s) by weight with respect to 100 parts by weight of EPDM. The molar ratio of addition is indicated by the molar ratio of peroxy bond. In Comparative Example 4, the heated material was cross-linked and it was impossible to measure the Mooney viscosity.

[0055]

The results in Table 2 suggests that when the peroxide having a hydroperoxy group and the radical generator having a 1-minute half-life temperature not higher than 195°C according to the present invention are used in a specific molar ratio (Examples 5 to 8), hydroxyl groups are efficiently introduced with Mooney viscosity almost the same as that of the material to which peroxide was not added (Comparative Example 3). In other words, it has been found that hydroxyl groups can be introduced almost without cross-linking or degradation.

When a radical generator is added in such an amount that more than 1 mole of the radical generating groups are present with respect to 1 mole of the hydroperoxy groups of the peroxide having a hydroperoxy group, cross-linking remarkably progressed (Comparative Example 4).

[0056]

Example 9

Using a Banbury mixer, 50 parts of PP, 50 parts of hydroxyl-modified EPM (EPM-1) obtained in Example 1 and 0.1 part of IRGANOX 1010 (antioxidant) were kneaded under conditions of a rotation number of 100 rpm and 170°C for 10 minutes. The kneaded material was subjected to press molding at 180°C to obtain a plate-like test piece. After wiping the surface of the test piece with trichloroethane, two-component urethane coating (available from BASF NOF Coatings Co., Ltd., product name: High-Urethane No. 5000) was coated thereon in a film thickness of about 60 μm, and the coating was baked under a condition of 120°C × 20 minutes to dry. Further, after leaving the coated material at room temperature overnight, 100 cross cuts of 1 mm by 1 mm were made in the formed coating and a piece of scotch tape was adhered thereon. When the tape was peeled off, peeling of the cross-cut coating was not observed.

[0057]

Comparative Example 5

Experiment was conducted in accordance with Example 9 except that non-modified EPM was used instead of EPM-1 in Example 9. As a result, all pieces of the cross-cut coating peeled off.

[0058]

Example 10

Experiment was conducted in accordance with Example 9 except that the hydroxyl-modified EPDM (EPDM-5) obtained in Example 5 was used instead of hydroxyl-modified EPM in Example 9. As a result, peeling of the cross-cut coating was not

observed.

[0059]

Comparative Example 6

Experiment was conducted in accordance with Example 10 except that non-modified EPDM was used instead of EPDM-5 in Example 10. As a result, all pieces of the cross-cut coating peeled off.

[0060]

Comparison of the results of Example 9 and Comparative Example 5 suggests that the polypropylene resin composition containing the hydroxyl-modified EPM of the present invention has an excellent coating adhesion property.

Comparison of the results of Example 10 and Comparative Example 6 suggests that the polypropylene resin composition containing the hydroxyl-modified EPDM of the present invention has an excellent coating adhesion property.

[0061]

[Advantages of the Invention]

As discussed above, the method according to the present invention easily and efficiently produces a hydroxyl-modified ethylene-□-olefin copolymer without cross-linking or degrading an ethylene-□-olefin copolymer.

In addition, the hydroxyl-modified ethylene-□-olefin copolymer according to the present invention is excellent in coatability and adhesiveness.

Accordingly, the present invention has a great deal of potential in industry.

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[Name of Document] Abstract

[Abstract]

[Objective]

To provide a method for easily and efficiently producing a hydroxyl-modified ethylene-α-olefin copolymer without cross-linking or degrading an ethylene-α-olefin copolymer, which is a starting material, and to provide a hydroxyl-modified ethylene-α-olefin copolymer excellent in coatability and adhesiveness.

[Means for Solving Problems] A hydroxyl-modified ethylene-α-olefin copolymer production method in which an ethylene-α-olefin copolymer is heated in the presence of a peroxide having a hydroperoxy group. The method being characterized by mixing 0.1 to 20 parts by weight of the peroxide having a hydroperoxy group with respect to 100 parts by weight of an ethylene-α-olefin copolymer; and the heating temperature being between a 10-hour half-life temperature and a 1-minute half-life temperature of the peroxide.

[Selected Drawing] None